

Coexistence of spin-singlets and metallic behavior in simple cubic CsC₆₀

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(Dated: February 1, 2008)

We present a detailed NMR study of simple cubic CsC₆₀, the only metallic cubic fullerides known so far besides A₃C₆₀. ¹³³Cs NMR signals the presence of about 12 to 15 % of “anomalous” C₆₀ balls, characterized by a 15 meV gap. We present different experimental observations supporting the idea that a spin-singlet (i.e. a C₆₀²⁻) is localized on these latter balls and stabilized by a JTD. A splitting of the ¹³³Cs spectrum into three different lines, with distinct electronic environments, is observed which emerges naturally from such a situation. Quadrupole effects on ¹³³Cs confirm an inhomogeneous distribution of the charge between C₆₀ molecules. Analysis of the relative intensities of the ¹³³Cs lines show that the spin-singlets do not form clusters at the local scale, but are diluted within the lattice. This is probably to avoid the occurrence of neighboring C₆₀²⁻ and minimize electrostatic repulsion between these balls. Through spin-lattice relaxation measurements, we detect chemical exchange between the Cs sites above 100 K. From this, we deduce that the lifetime of a spin-singlet on a given ball decreases exponentially with increasing temperature (from 15 sec at 100 K to 3 ms at 130 K). The implications of the presence of such spin-singlets for the nature of the metallic state is discussed, in relation with a decrease of 1/T₁T for ¹³C at low temperatures, which would be anomalous for a simple metal.

PACS numbers:

I. INTRODUCTION

To investigate the electronic properties of fullerides, one would wish to vary freely the number of doped electrons between 0 and 6 in the triply degenerate t_{1u} band. It is rather difficult with chemical doping because only a limited number of phases appear to be stable. The FET devices recently synthesized¹ might offer a more convenient way to do this, as the number of charge carriers injected in one C₆₀ monolayer can be controlled through an applied gate voltage. However, although transport measurements are easily accessible, all investigations cannot be performed on these systems. Furthermore, it is not yet clear whether the properties of “bulk C₆₀” are similar to those of its surface² and a careful comparison between the two systems is extremely desirable. To achieve that, the number of chemically stable bulk stoichiometries has to be extended.

The conventional chemical doping is obtained by inserting n alkali ions (A) in the C₆₀ structure, leading to A _{n} C₆₀ compounds, where the charge state of the C₆₀ molecule is very close to $-n$. The direct influence of the alkali atoms on these properties are thought to be negligible, although it could be a complication in some cases, mainly through structural modifications. Usually, only phases with an integer number of electrons per ball are formed. A₃C₆₀ and A₄C₆₀ were discovered first³ and were consequently the most studied. A₃C₆₀ are metals and superconductors at low temperatures, while A₄C₆₀ are insulators. As both should be metals in a simple band structure approach⁴, such a difference raises fundamental questions. Electronic correlation and/or electron

phonon coupling, both neglected in simple band calculations, must be important here. In view of the contrasted experimental situation, it seems important to extend investigations to other stoichiometries to estimate the relative importance of the different parameters. This paper is a second of a series of three papers devoted to this task, called hereafter I⁵, II and III⁶.

Certain stoichiometries are more difficult to obtain for the following reasons.

- $n=1$ is stable (with $A=K, Rb, Cs$) but spontaneously polymerizes below 350 K⁷, leading to a rich but different physics, where low dimensionality could play a role. To avoid this problem, the cubic fcc phase ($T > 350$ K) has been quenched to obtain metastable phases with cubic symmetry. A non-cubic phase is usually formed with C₆₀ dimers⁸. In the case of CsC₆₀ however, a cubic phase can be obtained by quenching to liquid nitrogen⁹, which is orientationally ordered (sc Pa $\bar{3}$ symmetry)¹⁰. It is called hereafter CQ for cubic quenched and the purpose of this paper is to study the electronic properties of this phase, which is predominantly metallic. On the other hand, the properties of the high temperature cubic phase will be discussed in paper III.

- $n=2$ is not obtained with large alkali ions (K, Rb, Cs) that first fill the large octahedral site (forming A₁C₆₀) and then the two tetrahedral sites (forming A₃C₆₀). Na₂C₆₀ is the only case where $n=2$ can be studied and we have shown that it behaves similarly to A₄C₆₀, i.e. there is a gap in the electronic structure¹¹. As these stoichiometries have symmetric positions in the t_{1u} band, this gap must be an intrinsic feature of these band fill-

ings. A detailed comparative NMR study of Na_2C_{60} and K_4C_{60} has been presented in paper I.

- $n=5$ cannot be reached by inserting only alkali ion. A charge transfer of 5 electrons per C_{60} has been observed in $\text{ABa}_2\text{C}_{60}$ ($A=\text{K}, \text{Rb}, \text{Cs}$) because Ba gives 2 electrons to the C_{60} ¹². The t_{1u} band might be modified in this case by some hybridization with Ba orbitals. We note that the first investigations indicate a metallic state, Korringa law has for example been observed by NMR¹ although more studies are still necessary.

This short review suggests that, beyond the opposition of A_3C_{60} and A_4C_{60} , compounds with an *even* number of electrons per C_{60} are insulators, while those with an *odd* number of electrons are metals. This is puzzling as, if the band picture fails because the Coulomb repulsion $U \approx 1$ eV is larger than the bandwidth $W \approx 0.5$ eV, but, a compound with an integer number of electrons should be Mott insulators. The study presented here reveals the presence in CQ CsC_{60} of a small number of C_{60}^{2-} . This implies that there must be an effective attractive interaction at the local scale that helps in this case to overcome the strong Coulomb repulsion. Understanding the actual mechanism for the formation of such pairs is then likely to shed new light on how some of these phases can become metallic despite the large Coulomb repulsion. We will argue that a Jahn-Teller distortion (JTD) of the C_{60} molecule, which is a consequence of the electron-phonon coupling in these systems with degenerate bands, is the missing ingredient responsible for this behavior.

The difficulties introduced by the quench necessary to produce CQ CsC_{60} have limited so far experimental investigations, for example there are no reported transport measurements. Also, the available temperature range is restricted to $T < 135$ K, above which it transforms irreversibly into the dimer phase. The CQ phase appears to be metallic as ESR detects a Pauli-like susceptibility⁹ and ^{13}C NMR spin-lattice relaxation follows a Korringa law down to 50 K¹⁴. By analogy to A_3C_{60} , a superconducting ground state could be expected, but no superconductivity has been detected down to 4 K⁹. We have suggested in ref.¹⁴ that it could be due to a competition with alternative ground states. Indeed, clear anomalies in the ^{133}Cs NMR spectrum indicate that *the electronic properties of CQ CsC_{60} are not homogeneous on the local scale*. The situation can be summarized by the picture of Fig. 1. Within a predominantly metallic phase, we proposed that 2 electrons get localized on some C_{60} balls (about 10 %) and paired into a spin-singlet. We will give in this paper new experimental observations which support this scenario (section II). To get more detailed information on this charge segregation phenomenon, we particularly focus our attention in this paper on some features that were not addressed in our previous report on this phase¹⁴: the distribution of the C_{60}^{2-} within the metal (section III) and their lifetime (section IV). Finally, we discuss the implications of the presence of C_{60}^{2n-} for the nature of the metallic state (section V).

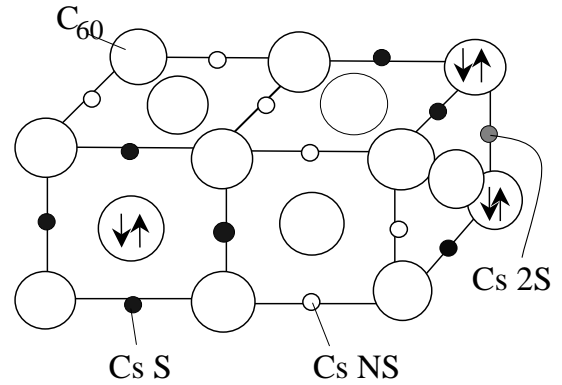


FIG. 1: Structural model of cubic quenched CsC_{60} describing the electronic properties as revealed by NMR. Spin-singlets are localized on a fraction of the C_{60} balls (about 10%) leading to different types of Cs sites. They are called respectively NS, S or 2S when 0, 1 or 2 of the 6 C_{60} neighbors of one Cs site bears a singlet. The remaining electrons are delocalized over the other C_{60} balls.

II. THREE CS LINES

On the ^{133}Cs spectrum of Fig. 2, obtained at 120 K and 7 T, three different lines are clearly resolved at -15 ppm, 800 ppm and 1800 ppm. The latter line has a much smaller intensity ($6 \pm 2\%$ of the total) than the two main lines and was not detected in ref.¹⁴. As shown hereafter, its detection allows to confirm and refine the model of Fig. 1.

Finding three Cs lines contradicts the expectations of structural studies, for which there is only one site for Cs in this phase, namely the octahedral site¹⁰. With one site, only one NMR line should be observed, as in the high temperature *fcc* phase¹⁵. The particular phase diagram of CsC_{60} allows to convince oneself rather directly that all these lines are intrinsic, because they all disappear irreversibly at the transition to the dimerized structure. In addition, SEDOR experiments reported in ref.¹⁴ demonstrate that the different Cs sites are mixed on the microscopic scale.

A. Local electronic environment of the three Cs lines

The splitting of the ^{133}Cs NMR spectrum implies that there are three different Cs sites well defined at the local scale. To understand their origin, the study of the local electronic environment, as probed by the NMR shift K and the spin-lattice relaxation rate $1/T_1$ of each line, both presented in Fig. 3, is very helpful. These quantities depend on the hyperfine coupling A between Cs and one of its 6 C_{60} first neighbors. The shift is expected to read $K = \sigma + 6A\chi_{loc}$, where σ is the reference chemical shift and χ_{loc} the local electronic susceptibility, and $1/T_1 \propto 6A^2\chi''_{loc}(\omega_0)/\omega_0$, where $\chi''_{loc}(\omega_0)$ is the imaginary

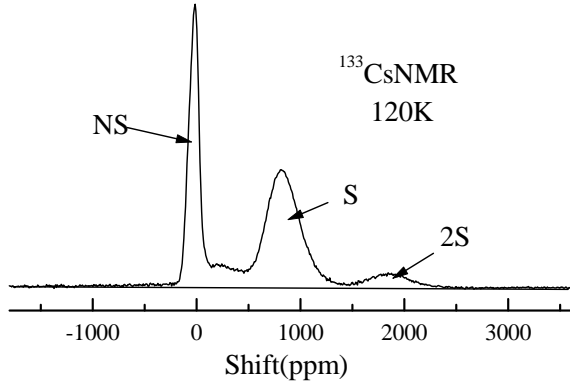


FIG. 2: ^{133}Cs NMR spectrum at 120 K in the cubic quenched phase showing the different Cs lines. The repetition time was 200 msec.

part of χ_{loc} at the nuclear Larmor frequency (for ^{133}Cs , $\omega_0 = 40$ MHz at 7 T). The reference chemical shift can be estimated by the position of Cs^+ in the gas phase to be around $\sigma = -300$ ppm¹⁶. Therefore, the shift of the less shifted line is small, about 200 ppm at low temperature, and we label this line as NS for Not Shifted. Such a small shift is expected for Cs in metallic fullerenes because electrons are almost completely transferred to the C_{60} balls. In addition, it is almost temperature independent according with a metallic susceptibility (the upturn above 100 K will be discussed in section IVb). On the contrary, the two other lines exhibit unusually large shifts with large temperature dependences inconsistent with a metallic environment. To contrast with the NS line, the line at 800 ppm is called S (for shifted). Interestingly, the shift of the most shifted line is approximately twice that of the S line and we therefore label it 2S. Similarly its T_1 is reduced by a factor 2 with respect to that of the S line. At 80 K, $^{25}\text{T}_1 = 43\text{ms} \pm 11\text{ms}$ to be compared with $^{5}\text{T}_1 = 110 \pm 10$ ms for the S line.

These latter points strongly suggests that *the inequivalency between the Cs sites results from a local perturbation and that the three lines emerge from the coupling with zero (NS), one (S) or two (2S) “anomalous C_{60}^- ”*. Indeed, if we call χ_g and χ_m the susceptibilities of respectively one “anomalous C_{60}^- ” and one “metallic C_{60}^- ”, A_g and A_m the hyperfine couplings between them and Cs, we expect the following relations.

$$\begin{aligned} K_{NS} &= 6A_m\chi_m & 1/T_1)_{NS} &\propto 6A_m^2\chi_m'' \\ K_S &= 5A_m\chi_m + A_g\chi_g & 1/T_1)_S &\propto 5A_m^2\chi_m'' + A_g^2\chi_g'' \\ K_{2S} &= 4A_m\chi_m + 2A_g\chi_g & 1/T_1)_{2S} &\propto 4A_m^2\chi_m'' + 2A_g^2\chi_g'' \end{aligned}$$

This fits the experimental observations $K_{2S} \approx 2K_S$ and $1/T_1)_{2S} \approx 2 1/T_1)_S$ provided that the anomalous component dominates the metallic one, i.e $A_g \chi_g \gg A_m \chi_m$, which is obvious since $K_S \gg K_{NS}$. We can actually estimate $A_m \chi_m = 30$ ppm and $A_g \chi_g = 700$ ppm at 120

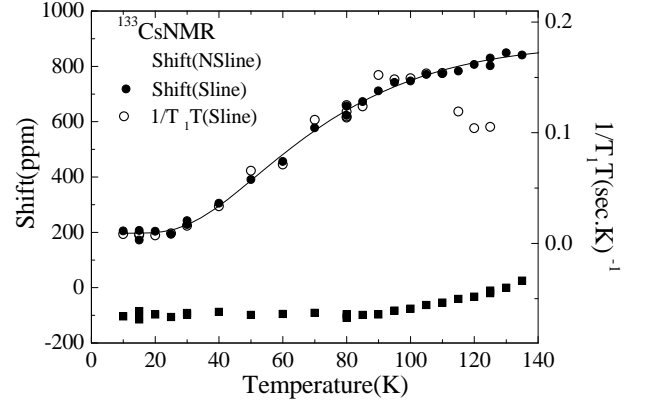


FIG. 3: ^{133}Cs NMR shifts with respect to a CsCl solution as a function of temperature for the two main Cs lines (NS and S) in cubic quenched CsC_{60} . For the S line, $1/T_1T$ is also displayed by open symbols (right scale). The line is a fit to a law $A+B/T \cdot \exp(-E_a/k_B T)$ with $E_a = 15$ meV.

K.

Fig. 3 also shows that there is a scaling between K and $1/T_1T$ for the S line up to 110 K, which ensures that they are both dominated in this temperature range by the same electronic excitations. This common behavior represents χ_g and is fitted on Fig. 3 by an activated law $(A/T) \cdot \exp(-E_a/k_B T)$ with $E_a \approx 15$ meV. This means that the “anomalous C_{60}^- ” correspond to a molecular arrangement with a gap E_a and therefore electrons must be localized on these balls. The simplest idea would be that one electron is “trapped” by some defects, but in this case we should observe a paramagnetic behavior of this localized spin 1/2 at low temperatures, which we do not. The most plausible way to explain the vanishing susceptibility at low T is that *two* electrons are localized instead of one and paired up into a *singlet*. Molecular calculations¹⁷ indeed predicts that the singlet state wins over the triplet state (favored by Hund’s rules) for C_{60}^{2-} in the presence of a JTD. In our opinion, this gain of energy associated with JTD is at the origin of the formation of C_{60}^{2-} within the metal. We note that there might be an additional temperature independent contribution χ_0 to K as its low temperature value is very different from our estimation of $\sigma = -300$ ppm or from the shift of the NS line.

Na_2C_{60} is a natural reference for the NMR behavior of the JTD C_{60}^{2-11} . The gap measured on Cs S sites is much smaller than the 140 meV singlet-triplet gap of a C_{60}^{2-} measured through $1/T_1$ relaxation in Na_2C_{60} . The limited stability of the CQ phase in temperature ($T < 135$ K) does not really allow to probe the existence of molecular excitations of this high energy. This 15 meV gap more likely corresponds to excitations of the singlets towards the metallic band. We have seen in paper I that in Na_2C_{60} also, the low temperature behavior is governed by such band excitations. The fact that the spin-singlets cannot be viewed as an isolated entity might also explain

why K and $1/T_1$ seem to tend to a constant value different from zero at low temperatures. More details will be given in the last section of this paper on the interactions between the singlets and the band.

B. Confirmation of local charge segregation

This inhomogeneous distribution of the charge among the C_{60} balls will create electric field gradients (EFG) at the Cs S and 2S sites and since ^{133}Cs is a spin $7/2$, it should sense them through its quadrupole moment Q . Actually, we show hereafter that the larger linewidth of the S line ($\Delta\nu \approx 16 \text{ kHz}$ at half width) compared to the NS line ($\Delta\nu \approx 5 \text{ kHz}$) is due to larger quadrupole effects on these sites.

In presence of quadrupole effects, the different nuclear transition ($7/2 \leftrightarrow 5/2$, $5/2 \leftrightarrow 3/2$, etc) acquire different frequencies $\nu_0 \pm n \nu_Q f(\theta, \varphi)$, where n is the order of the transition, ν_Q a quadrupole frequency proportional to the strength of the EFG and the value of the quadrupole moment, and $f(\theta, \varphi)$ a function depending on the orientation of the EFG with respect to the NMR field. Eventually, if ν_Q is very large, the “satellite transitions” could be lost because they become very broad and only the central transition $1/2 \leftrightarrow -1/2$ is observed. This is not very likely for ^{133}Cs , because it has one of the smallest quadrupole moment of all nuclei. The lengths of the NMR pulses that optimize the signal should be different in this situation¹⁸. As this is not the case, we conclude that all the nuclear transitions are observed for all sites and the broadening of the spectrum is then a first order quadrupole broadening.

The value of ν_Q expected for the S sites in our model can be estimated by a direct calculations of the EFG, assuming point charges.

$$\nu_Q = \frac{3(1 - \gamma_\infty)eV_{zz}Q}{2I(2I - 1)\hbar} \quad \text{with} \quad V_{zz} = \frac{\partial^2 V}{\partial z^2}$$

where V is the electrostatic potential, I the nuclear spin and $(1 - \gamma_\infty)$ the Sternheimer antishielding factor¹⁶. The distribution of charges around one S site yields $\nu_Q \approx 6 \text{ kHz}$. The resulting lineshape depends also on the other principal values of the EFG, here we calculate $V_{xx} = V_{yy} = -1/2 V_{zz}$. A simulation of the spectra (for this powder sample, it has to be averaged on all possible orientations¹⁶) is shown on Fig. 4 in two different cases. For the dotted line, a very small experimental broadening is introduced and all satellite transitions are visible. For the thin line, a realistic experimental broadening of 3 kHz, similar to the NS linewidth, is introduced, which allows a direct comparison with the experimental spectrum. The agreement is very good which should only be taken as a proof of the consistency of our analysis. It is known that the EFG could vary significantly from this rough point charge estimate, when a more realistic situation is considered, for example an inhomogeneous distribution of the charge over the C_{60} molecule.

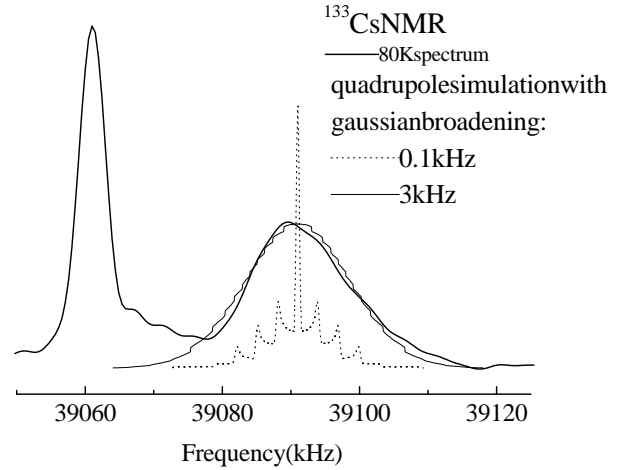


FIG. 4: ^{133}Cs spectrum at 80 K in the CQ phase (thick line). The other lines are quadrupole simulations of the S lineshape explained in the text. The theoretical lineshape is convoluted by a gaussian of linewidth 0.1 kHz (dotted line) and 3 kHz (thin line).

As for the 2S line, the linewidth is similar to that of S ($\Delta\nu \approx 18 \text{ kHz}$). This is consistent with the idea that the broadening is not of magnetic origin, for example arising from a distribution of shift, in which case the linewidth should double. The quadrupole broadening for a 2S site in our model depends on the relative position of the C_{60}^{2-} with respect to this Cs site. If they are on a straight line with respect to their common Cs neighbor, the point charge calculation predicts that $\nu_Q[2S] = 2 \nu_Q[S]$, while if they are in different directions $\nu_Q[2S] \simeq \nu_Q[S]$. This latter case would apparently be in better agreement with the data but, as already mentioned, the calculation of the EFG is somewhat rough and the lack of structure in the S and 2S lineshape does not allow a refined analysis. Actually, next section provides more reliable information on the distribution of the C_{60}^{2-} , which do not favor this arrangement.

The detection of quadrupole effects on S and 2S sites is however essential to ensure a qualitative agreement with the model of Fig. 1.

III. DISTRIBUTION OF THE C_{60}^{2-} WITHIN THE METAL

Following the lines of the model described in Fig. 1, the number of C_{60}^{2-} can be deduced from the relative intensities of the three lines, the area of one line being proportional to the number of sites resonating at this frequency. As can be seen on Fig. 5, the ratio between S and NS sites is nearly constant as a function of temperature, NS/S = 45/55, and it is reproducible with different samples and/or different quench, so that it must correspond to a well defined equilibrium. As there are 6 C_{60} neighbors to one Cs site, there must be roughly 10 % of

C_{60}^{2-} to produce this ratio. With such a number, there is a non-negligible probability of finding a Cs site with two C_{60}^{2-} neighbors, which correspond to our “2S sites”.

A. Structural arrangement of the C_{60}^{2-}

More precisely, a closer look at the relative intensities, and especially the number of 2S sites, can help us to address the question of the *distribution* of C_{60}^{2-} balls within the metal. On Fig. 6, we show the results of calculations of the number of Cs sites as a function of the concentration of C_{60}^{2-} in two different cases :

- i) with a random distribution of C_{60}^{2-}
- ii) when neighboring C_{60}^{2-} are excluded (“diluted” case).

To compare with the experiment, the number of S, NS and 2S sites at 120K are reported on Fig. 6. In the random case, the calculated intensities never quite reach the experimentally observed values. The fraction of 2S sites is rapidly higher than in the experiment and there are always more NS sites than S sites, contrary to the experiment. Furthermore, the intensity of a 3S line corresponding to C_{60} with three C_{60}^{2-} neighbors would be sizable, although it is not observed. In the diluted case, 12% of C_{60}^{2-} almost exactly correspond to the experiment at 120 K, as shown by the vertical line. In this situation, the 3S configuration is forbidden, according to the experimental finding. Therefore, we conclude that C_{60}^{2-} are diluted within the lattice to avoid a situation where they are first neighbors. They do not segregate in superstructures that could be reminiscent of the formation of stripes. This last point is consistent with SEDOR experiments that rule out the formation of “clusters” of C_{60}^{2-} . This dilution could be favored because it minimizes the

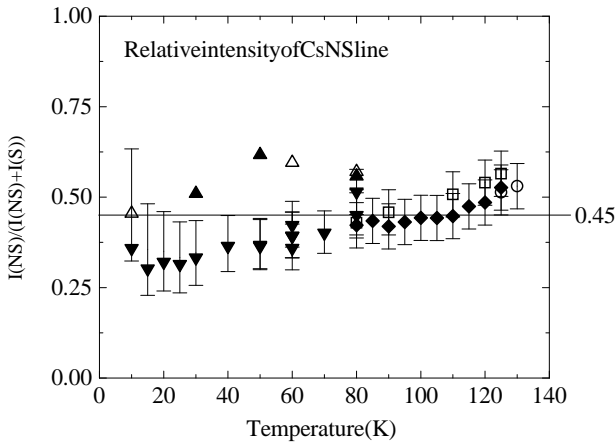


FIG. 5: Relative intensity of the ^{133}Cs NS line compared to the one of the S line. This gives the percentage of NS sites as a function of temperature. The different symbols refer to different samples and/or different quench, showing a good reproducibility of this measurement. Error bars are larger at low temperatures when the two lines begin to overlap.

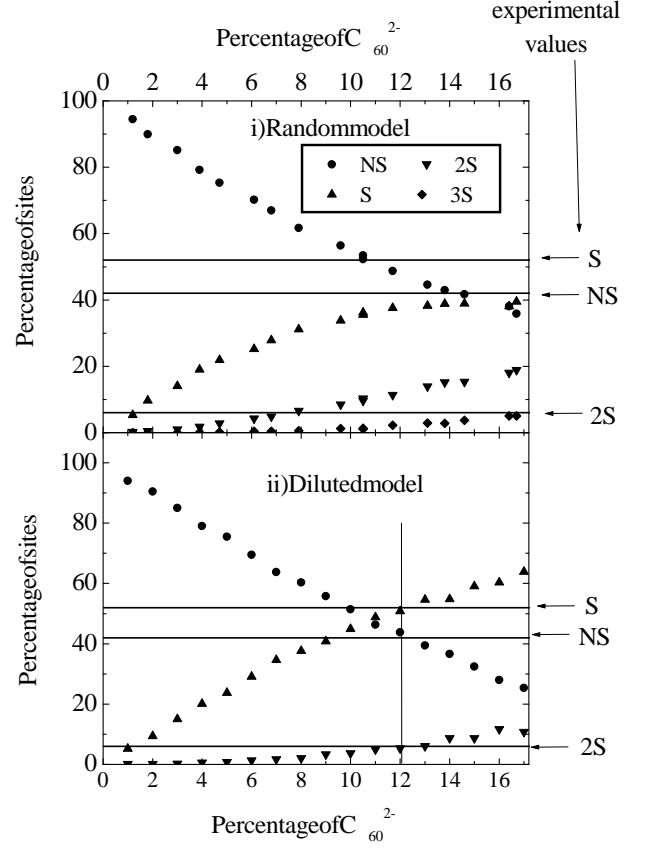


FIG. 6: Simulation of the number of NS, S, 2S and 3S Cs sites as a function of the percentage of C_{60}^{2-} in two different situations: i) the distribution of C_{60}^{2-} is assumed to be random, ii) a “diluted model” where two neighboring C_{60} molecules in a singlet state are excluded (in this case there are no 3S sites). Experimental values at 120 K are given by horizontal lines for comparison and the agreement with 12 % C_{60}^{2-} in the diluted case by a vertical line.

electrostatic repulsion between C_{60}^{2-} . As a function of decreasing temperature, comparison between Fig. 5 and Fig. 6 suggests an increase of the number of C_{60}^{2-} to about 15 %, although the error bars are quite large.

B. What limits the number of C_{60}^{2-} to about 10 to 15% ?

The experimental concentration of C_{60}^{2-} appears a little bit puzzling at first, since one could expect that if the C_{60}^{2-} are more stable than C_{60}^{-} , there should be a total charge dismutation between C_{60} and C_{60}^{2-} . One problem with such a dismutated ground state is that it *cannot* be realized in this phase because of the inherent frustration of the *fcc* lattice. Furthermore, if first neighboring C_{60}^{2-} are excluded, the maximum number of C_{60}^{2-} would already be reduced to 25 %. This would correspond to a completely ordered structure with a singlet on each corner of the cubic cell and none on the faces. With some

disorder, this number would rapidly drop.

Maybe the C_{60}^{2-} do not order collectively, because they are preferentially formed on some defects of the structure. A particular feature of the orientational order characterizing the *sc* phase is that there are two orientations for the C_{60} molecule. They are defined by an angle φ from which they are rotated with respect to the so-called “standard orientation” around one diagonal axis¹⁹. The value minimizing the C_{60} interactions occurs for $\varphi = 98^\circ$ but a second minimum for $\varphi = 38^\circ$ is nearly degenerate. The fit of the X-ray spectra can be improved in all *sc* phases (C_{60} , Na_2AC_{60} and $CQ\ CsC_{60}$) by allowing 12 to 20 % of the balls at low T to be in a “minor orientation” corresponding to $\varphi = 38^\circ$. For $CQ\ CsC_{60}$ 16 % gives the best fit at 4.5 K¹⁰. The closeness of this value with the number of singlets found here is such that one is tempted to consider that a ball in a minor orientation might be viewed as a disorder potential efficient in trapping a C_{60}^{2-} . It is indeed known that the overlap integrals between neighboring C_{60} are very sensitive to their relative orientations. In pure C_{60} , no structural correlations were found between the balls in a given orientation¹⁹, as found here for the singlets.

IV. MOTION OF SPIN-SINGLETS ABOVE 100 K

The observation of three different lines indicate that the spin-singlets are nearly static on well determined C_{60} balls on the NMR timescale. However we show hereafter that other experimental observations such as the NMR spin lattice relaxation time T_1 allow to determine the lifetime of the spin singlets which decreases with increasing temperature.

A. Relaxation behavior

As can be seen in Fig. 7, T_1 for the NS line changes dramatically between 110 K and 130 K, getting shorter by two order of magnitudes. At 130 K although the two main ^{133}Cs lines are perfectly resolved, they have almost the same T_1 . This finding suggests that the nature (NS, S or 2S) of any Cs nucleus is changing with time, so that the properties of these sites become identical on the large timescale of the T_1 measurement (more than 50 ms), although on the short timescale corresponding to the inverse spectrum width (typically 100 μs here), individual resonance frequencies are still resolved. Within our model, such a situation would occur if the electronic spin-singlets start to jump from a C_{60} to its near neighbor C_{60} . When such an electronic jump occurs, some Cs S sites become NS and vice-versa.

Let us examine in more details whether a motion of the spin-singlets could explain the change in T_1 ²⁰. We assume that there is a probability p per unit time that the nature of the site changes from S to NS or NS to S.

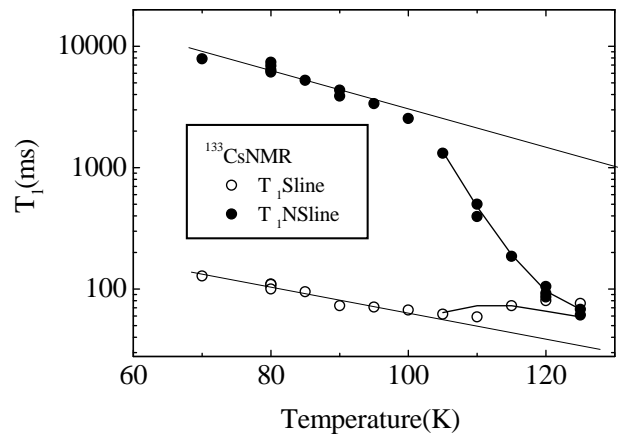


FIG. 7: T_1 for the two main ^{133}Cs NMR lines between 80 K and 135 K. The reduction of the NS line T_1 for above 100 K is attributed to chemical exchange between the two sites. The straight lines extrapolate the temperature evolution of T_1 if there were no exchange. The other lines are a fit to our model of chemical exchange (see text).

On the other hand, we suppose that for each situation (Cs neighboring a C_{60}^{2-} or not), there is a well defined relaxation rate W_S (resp. W_{NS}). Let n_S be the number of S sites (resp. n_{NS} for NS sites) excited at the time $t=0$ by the saturation pulse of the T_1 experiment, the relaxation of the two spin species obeys the following coupled system.

$$\begin{aligned} \frac{dn_S}{dt} &= -(W_S + p) n_S + p n_{NS} \\ \frac{dn_{NS}}{dt} &= p n_S - (W_{NS} + p) n_{NS} \end{aligned}$$

For an infinite lifetime of the singlets, that is for $p = 0$, we recover the expected exponential decay with $(1/T_1)_S = W_S$ and $(1/T_1)_{NS} = W_{NS}$. When $W_{NS} \leq p \leq W_S$, the relaxation rate of the NS line is strongly

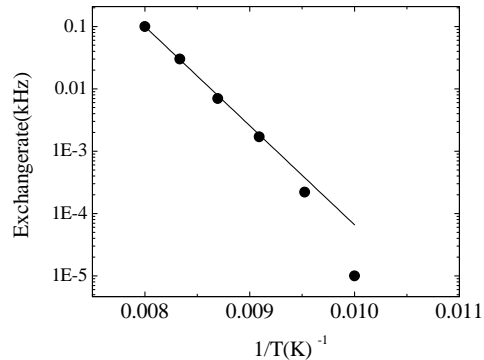


FIG. 8: Logarithmic plot of the value of the exchange parameter p used to obtain the line of Fig. 7 as a function of the inverse of the temperature. p can be fitted by an activated law as shown by the solid line.

reduced and tend to the value $(W_S + W_{NS}) / 2$ as p increases. By extrapolating the variation of W_S and W_{NS} by straight lines (see Fig.7), we calculate with this model the value needed for p to obtain the experimental T_1 values. We can indeed reproduce the experimental results, as shown by the dashed lines on Fig. 7. For each temperature, the value of p that we have used is reported on Fig. 8. It follows an activated temperature dependence with $p = 5 \cdot 10^{14} \cdot \exp(-3700/T)$, which sets a new energy scale for the system of about 320 meV, characterizing the energy barriers that traps the singlet. This magnitude is quite comparable with the activation energies usually found for the molecular rotations in A_nC_{60} compounds. The temperature range where we start to observe the motion of the spin-singlets also roughly corresponds to the usual range for the onset of molecular motions. This reinforces the idea that the trapping of the singlets could be related to C_{60} in a minor orientation.

From the frequency of jumps between the two sites, we can deduce the characteristic lifetime of a spin-singlet on a particular C_{60} ball. It changes from 15 sec at 100 K to 3 ms at 130 K.

B. Static spectrum

This characteristic time is still long compared to the time scale of the experiment, therefore the motions of the singlets do not show up clearly on the static spectra. However, in the range of temperatures for which the T_1 become identical, the scaling between the shift and the relaxation for the S line does not hold anymore (Fig. 3), which suggests that the jumps of the singlets begin to affect as well the resonance frequencies. If we could increase the temperature further, we could expect that p will become short enough to yield a *motional narrowing* of the static spectrum with three lines ultimately merging into one. From the data of Fig. 8, we can extrapolate that the two main lines would merge together at 150 K, when the frequency jump is comparable to the 30 kHz frequency separation of the two lines. This is a first step to reconcile the properties of CsC_{60} in its CQ and high temperature phases, where only one Cs line is observed. The relation between these two cubic phases will be discussed in more details in paper III. The upturn of the NS shift above 110 K that can be noted on Fig. 3 might be a precursor sign of this effect.

V. INTERPLAY BETWEEN THE SPIN-SINGLETS AND THE METALLIC STATE

The motion of spin-singlets described above shows that they can be considered to some extent as charge carriers. Actually, in a random metallic state with negligible on site Coulomb repulsion and nominally one electron per C_{60} , one expects to find on each C_{60} either zero, two or one electron, either with spin up or down, all states

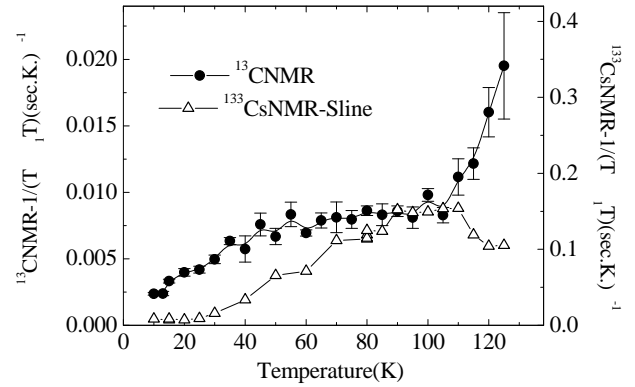


FIG. 9: $1/T_1T$ as a function of temperature for ^{13}C NMR (left scale) and ^{133}Cs NMR S line (right scale) in the CQ phase of CsC_{60} . While the ^{133}Cs S line behavior mainly reflects the properties of the gapped C_{60}^{2-} ion, ^{13}C NMR is dominated by the metallic behavior which becomes anomalous below 50 K.

with equal probabilities. A 25 % concentration of doubly charged C_{60} , or less if we include some Coulomb repulsion, is then quite natural and it is more their increased lifetime that is surprising here. We assign it to the higher stability of the JTD C_{60}^{2n-} , and this could play a particular role in the charge transport of $A_{2n+1}C_{60}$. In the presence of any disorder potential, they could become easily trapped, which seems to be the case in CQ- CsC_{60} .

An important question that has been left aside so far is whether there is also 12 % of static neutral C_{60} or if the unpaired electrons are delocalized on the 88% remaining balls. Although hypothetical, the possible “non-stoichiometric” of the CQ phase is reminiscent of the discussions about the role of vacancies in A_3C_{60} . The physical model behind this idea was that A_3C_{60} would be a Mott insulator for integer filling because of the strong electronic correlations and that only the deviation from 3, introduced by a reproducible number of vacancies, allows the formation of a metal²¹. The same argument could be discussed for CQ CsC_{60} .

From the experimental point of view, we are not able to distinguish by ^{13}C NMR the signals of differently charged C_{60} balls, neither the signal of C_{60}^{2-} or of any eventual neutral C_{60} , from that of the dominant fraction of C_{60}^- . This results from the well known fact that the anisotropic orbital contribution to the NMR shifts dominates the electronic contribution to the shift in A_nC_{60} compounds and broaden the signals at low temperatures²². Although different relaxation times could be expected for the different components, it is beyond experimental accuracy to detect such a small fraction of distinct behaviors. The relaxation curves for the NMR magnetization, from which T_1 is extracted, are intrinsically not exponential at low temperatures in fullerides, because of the existence of inequivalent ^{13}C sites on a given molecule⁵. This would easily blur the occurrence of different relaxation mechanism for a small fraction of the C_{60} .

Nevertheless, we do observe an anomaly in ^{13}C NMR,

which could help us to understand the coupling between the band and the formation of C_{60}^{2-} . Fig. 9 shows that although $1/T_1T$ is constant between 50 K and 100 K as expected for a metallic Korringa law, it decreases below 50 K by a factor ≈ 3 (the upturn above 100 K will be discussed in paper III). As emphasized on Fig. 9, this decrease is not correlated with the ^{133}Cs NMR for which $1/T_1T$ saturates precisely below 50 K and therefore more likely affects the properties of the band that dominate anyway the ^{13}C NMR. The Korringa law relates $1/T_1T$ to the square of the density of states ($1/T_1T \propto n(E_f)^2$) which suggests a decrease in the density of states at low T , that could be due to an increase in the number of C_{60}^{2-} , taking more electrons out of the band. The general trend of the variation of the number of C_{60}^{2-} indicated by Fig. 5 is in qualitative agreement with this idea but not quantitatively. The maximum variation of the number of NS sites between 50 K and 10 K would be from 50 % to 25 %, corresponding to an increase in C_{60}^{2-} from 12% to 17 % (see Fig. 6b) and then a decrease of $n(E_f)$ by about only 5 %. If the decrease of $1/T_1T$ is related to this effect, the properties of the band must be modified at the same time, for example $1/T_1T$ can be enhanced above the value expected from $n(E_f)$ by correlation effects¹⁶. Actually this effect exists in CQ CsC_{60} , as the constant value of $1/T_1T$ is enhanced by almost a factor 2 compared to $\text{Na}_2\text{CsC}_{60}$ that has a similar susceptibility and this could change as one goes further away from integer filling.

VI. CONCLUSION

We have shown that many independent NMR observations support the idea that spin-singlets are present in the CQ phase of CsC_{60} on about 12 % of the C_{60} balls. The lifetime of these spin-singlets on a given ball increases exponentially with decreasing temperature (from 3 ms at 130 K to 15 sec at 100 K). We believe that they are formed randomly by hopping within the metallic phase and become trapped at low temperatures, maybe by the disorder potential associated with the existence of two different orientations for the C_{60} molecules in the *sc* phase.

The most important consequence of this study is that it reveals an *attractive interaction at the local scale* which allows to form spin-singlets despite the large Coulomb repulsion that should forbid a double occupancy of the same site. We propose that this interaction is mediated by Jahn-Teller distortions. Because the gain of energy associated with a JTD is larger for an evenly charged

molecule, these configurations could be stabilized even in compounds with odd stoichiometries. It is natural to wonder whether this also plays a role in the case of A_3C_{60} .

The unexpected splitting of the ^{133}Cs spectrum, which is the consequence of the presence of C_{60}^{2-} , inevitably refers to the T' line observed in many *fcc* A_3C_{60} systems for the alkali in the tetrahedral site²³. SEDOR experiments have shown that the T' line arises from a modified tetrahedral site. Its intensity reproducibly corresponds to about 15 % of the tetrahedral sites. Many explanations have been proposed for the origin of the T' site (T' could be neighbor from a vacancy, a misoriented C_{60} or a JTD one etc.) but none of them is consistent with all experimental observations. By analogy to CQ CsC_{60} where the splitting is much clearer, it is tempting to say that the T' line could correspond to a small fraction of about 3 % localized C_{60}^{2-} or C_{60}^{4-} in A_3C_{60} , maybe trapped by some defects. We have suggested that the *sc* structure efficiently traps the C_{60}^{2-} on the balls in the minor orientation and the absence of such orientations in the *fcc* A_3C_{60} compounds might play a role. To check this, it would be interesting to know whether there is a similar line in the orientationally ordered $\text{Na}_2\text{CsC}_{60}$ and what is its intensity. This might be a clue to prove that the peculiar properties of CQ CsC_{60} actually reveal a common tendency in alkali fullerides.

Indeed, an independent NMR observation, based on an anomalous temperature dependence of $1/T_1T$, has recently led us to suggest that C_{60}^{2-} and C_{60}^{4-} are also formed in A_3C_{60} but usually on very short lifetimes of the order of 10^{-14} sec. We have proposed this idea by studying $\text{Na}_2\text{CsC}_{60}$ ¹¹ and we will present in paper III a generalization of this phenomenon to other systems like Rb_3C_{60} . The main difference between CQ CsC_{60} and these other compounds then resides in the *lifetime* of the C_{60}^{2n-} . In addition to the structural effect discussed before, this could be related to the fact that neutral C_{60} is not stabilized by JTD, so that a jump of one electron is less likely to lead to a stable configuration than in A_3C_{60} , which has a symmetric position between C_{60}^{2-} and C_{60}^{4-} . The different lifetime of the electronic pairs formed via Jahn-Teller distortions might also explain why CQ CsC_{60} is not superconducting contrary to A_3C_{60} . The difference of behavior should vanish as one increases the temperature and the singlets start to move more freely. Above 300 K, CsC_{60} can be studied again in a cubic structure, but, unexpectedly, it appears to be insulating. We will show new data at high temperature in paper III that allow to conclude that this behavior can be understood by taking into account the presence of C_{60}^{2-} and is in fact similar to that of some A_3C_{60} systems.

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